Electrochemically Responsive Self-Formed Li-ion Conductors for High Performance Li Metal Anodes

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June 20, 2018

Project ID: bat330

Overview

Timeline

- Project start date: October 1, 2016
- Project end date: September 30, 2019
- Percent complete: 50%

Budget

- Total project funding
  - DOE share: $1,139,319
  - Contractor share: $126,733
- Funding received in FY 2018
  - $784,594
- Funding for FY 2019
  - $354,725

Barriers

- Li dendrite growth
  - Microscopically uneven current density;
  - Safety issues;
  - Li continuous reaction with electrolyte.
- Low Coulombic efficiency
  - Large volume change;
  - Instability of SEI layers;
  - Consumption of electrolyte

Partners

- Project lead
  - PSU
- Interactions/collaborations
  - PNNL

Relevance/Objectives

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Objectives

- Develop an electrochemically responsive self-formed hybrid Li-ion conductor as a protective layer which allows high Coulombic efficiency (CE) (> 99.7%) and long dendrite-free cycling of Li metal for Li-S batteries.
- The Li-S battery cells with high energy densities will be delivered using Li metal anodes with this protective layer.

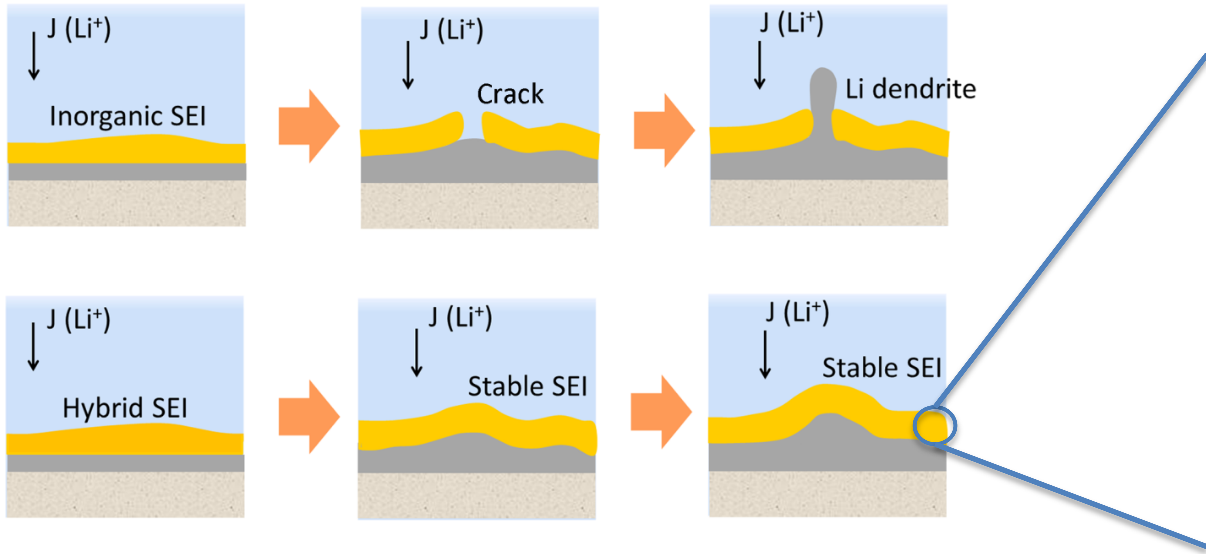
Impacts

- Self-formed ion-conducting protective layers will stop lithium dendrite growth, prevent continuous SEI growth and enable cycling lithium metal with high CE and long cycle life.
- The new ion-conducting protective layers will enable higher-energy-density, longer-cycling, safer Li-S batteries for electric vehicles.
- Meeting the technical targets will potentially develop a new high-energy-density Li battery, promote increased adoption of electric and plug-in hybrid electric vehicles (EVs and PHEVs).

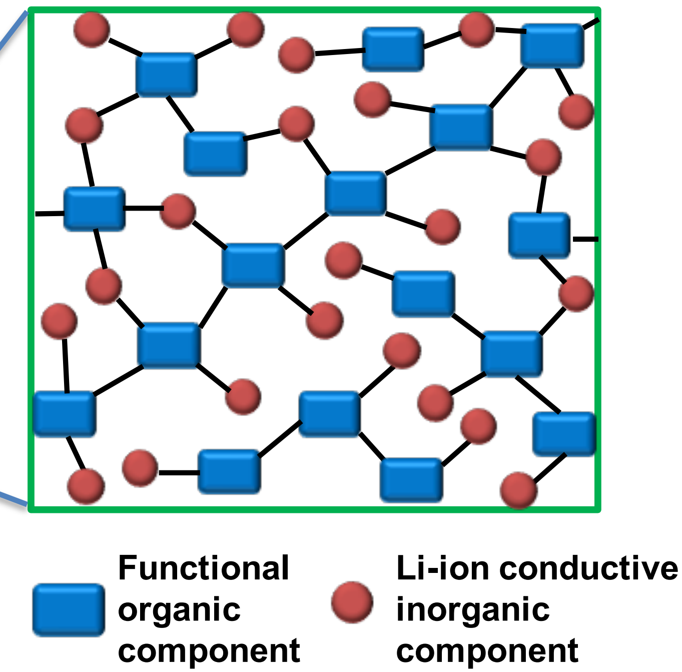
Milestones

Date	Milestones	Status
December 2017	Development of the 2nd generatin of organo-Li_xS_y lithium protection layers with tuned functionality. Conduct characterization and performance tests on the materials.	Complete
May 2018	Demonstrate the uniform and dendrite-free Li deposition under the protection of 2nd generation organo-Li_xS_y lithium protective layers.	On track
September 2018	Optimize 2nd generation organo-Li_xS_y lithium protective layer and demonstrate Li anodes cycling with ~98.8% CE for ~200 cycles.	On track
December 2018	Demonstrate Li anodes with optimized 2nd generation organo-Li_xS_y lithium protective layer and ~99.2% CE for ~300 cycles.	On track

Approach/Strategy



Organic-Inorganic Hybrid



Develop novel multiphase inorganic-organic hybrid ion conductors with tunable multifunctional organic components and controlled inorganic components, and thus enable safe use of lithium metal with high Coulombic efficiency.

- The organic components in the hybrid can decompose to spontaneously form an artificial SEI.
- The inorganic components can provide Li-ion conducting channels and good stiffness to enable mechanical robustness.
- The organic/inorganic hybrid can enable robust protection of Li metal anodes with high CE of lithium deposition/dissolution.

Technical Accomplishments and Progress

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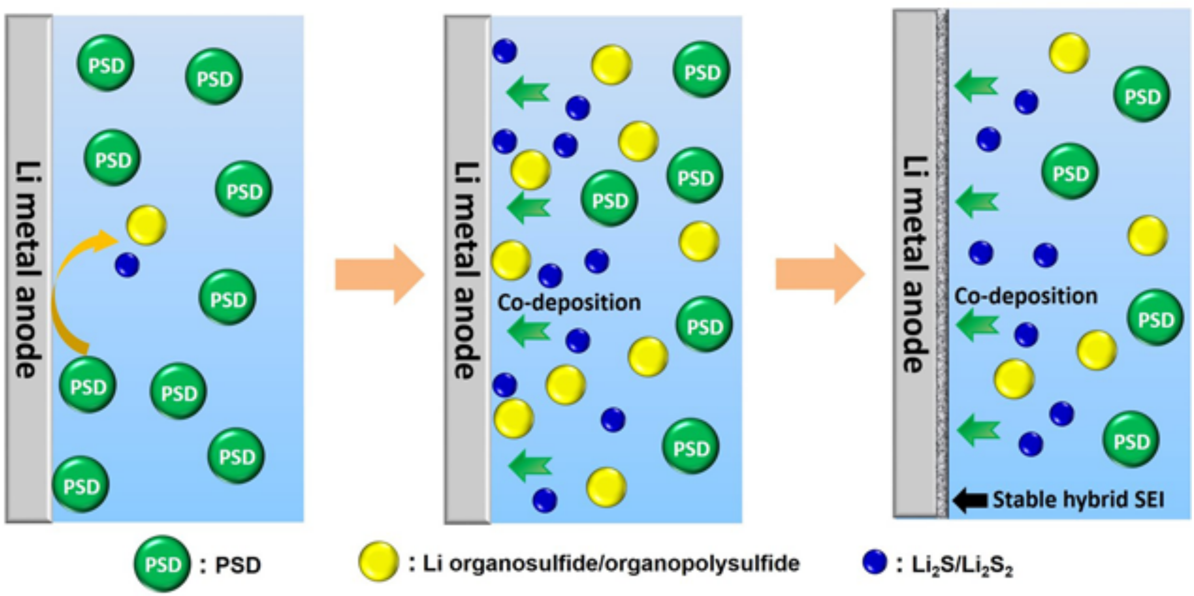
1. Li metal anodes

Organosulfide plasticized SEI layer on Li metal



PSD: the 2nd generation of sulfur containing polymer

Stable SEI layer
Uniform Li deposition

High CE

Technical Accomplishments and Progress

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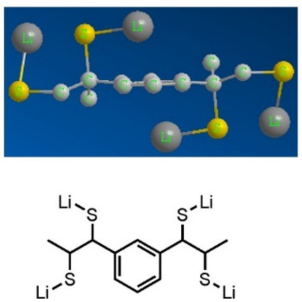
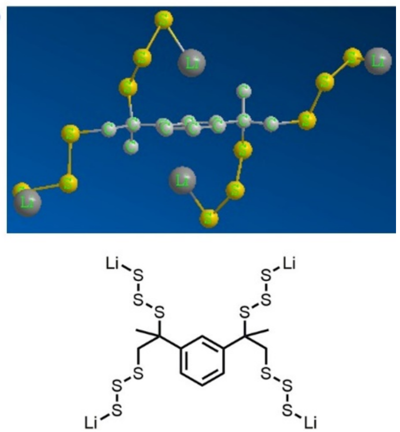
The 2nd generation of organo-Li_xS_y additive for Li protection layers

a



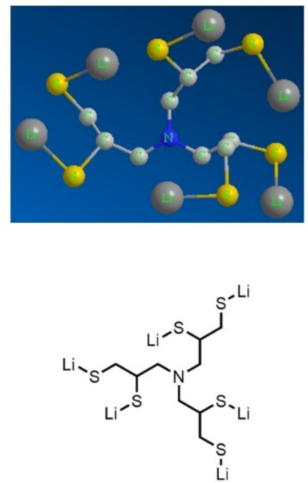
Aromatic-baded Li organosulfide from PSD

b



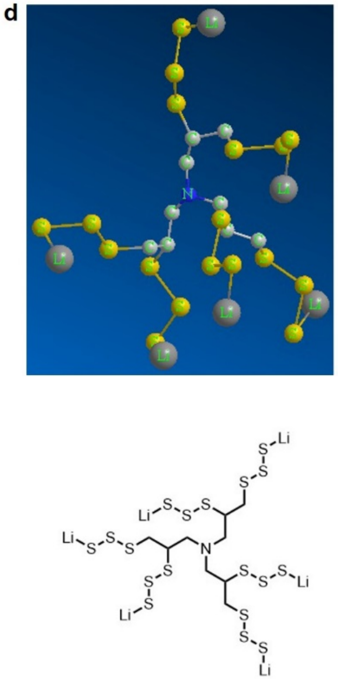
Aromatic-based Li organopolysulfide from PSD

c



Alkyl amine-based Li organosulfide from PST

d



Alkyl amine-based Li organopolysulfide from PST

2nd generation: aromatic-based organic components

1. **planar backbone conformation**
2. **π-π interaction**

1st generation

Technical Accomplishments and Progress

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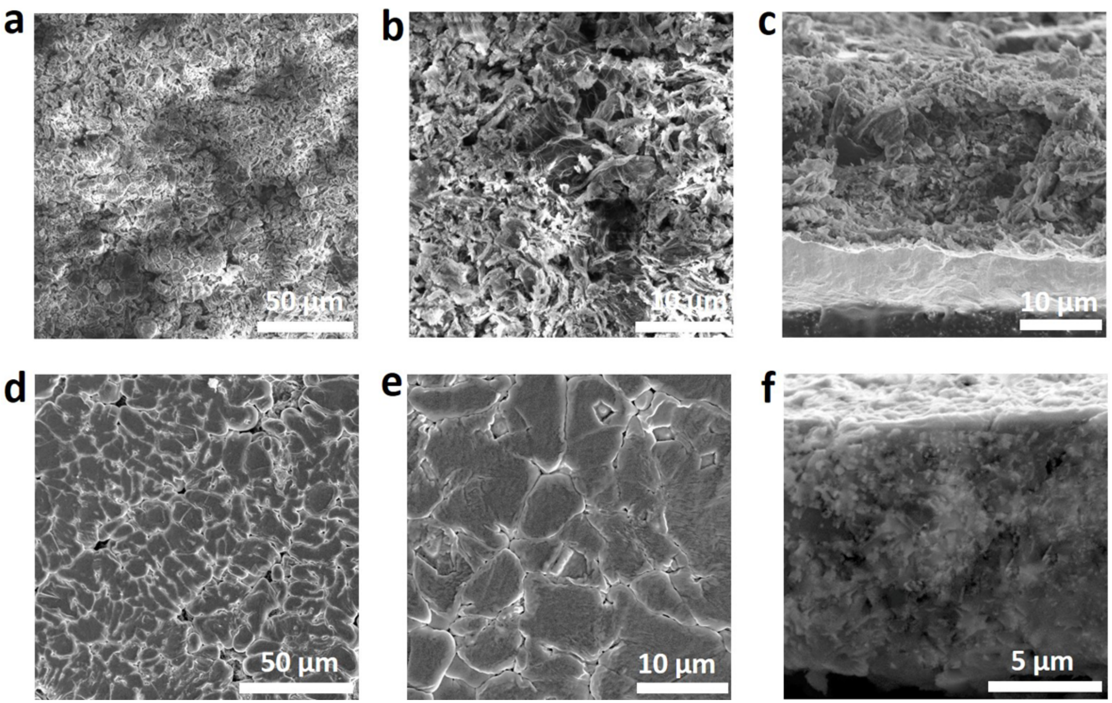
The 2nd generation of organo-Li_xS_y protection layer for Li metal

Li Morphology after 10 cycles

Control electrolyte



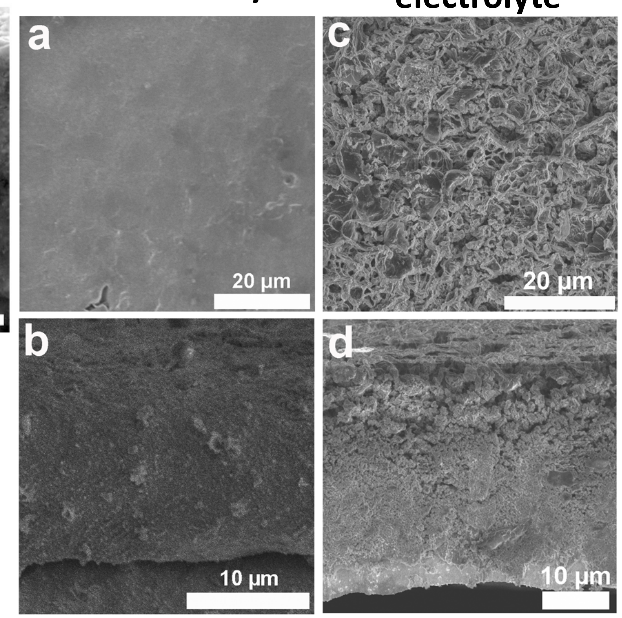
PSD electrolyte

Current density: 2 mA cm^{-2}
Capacity: 2 mA h cm^{-2}

Morphology of SEI layers after 100 cycles

PSD electrolyte

Control electrolyte



Top view

Cross-section

Technical Accomplishments and Progress

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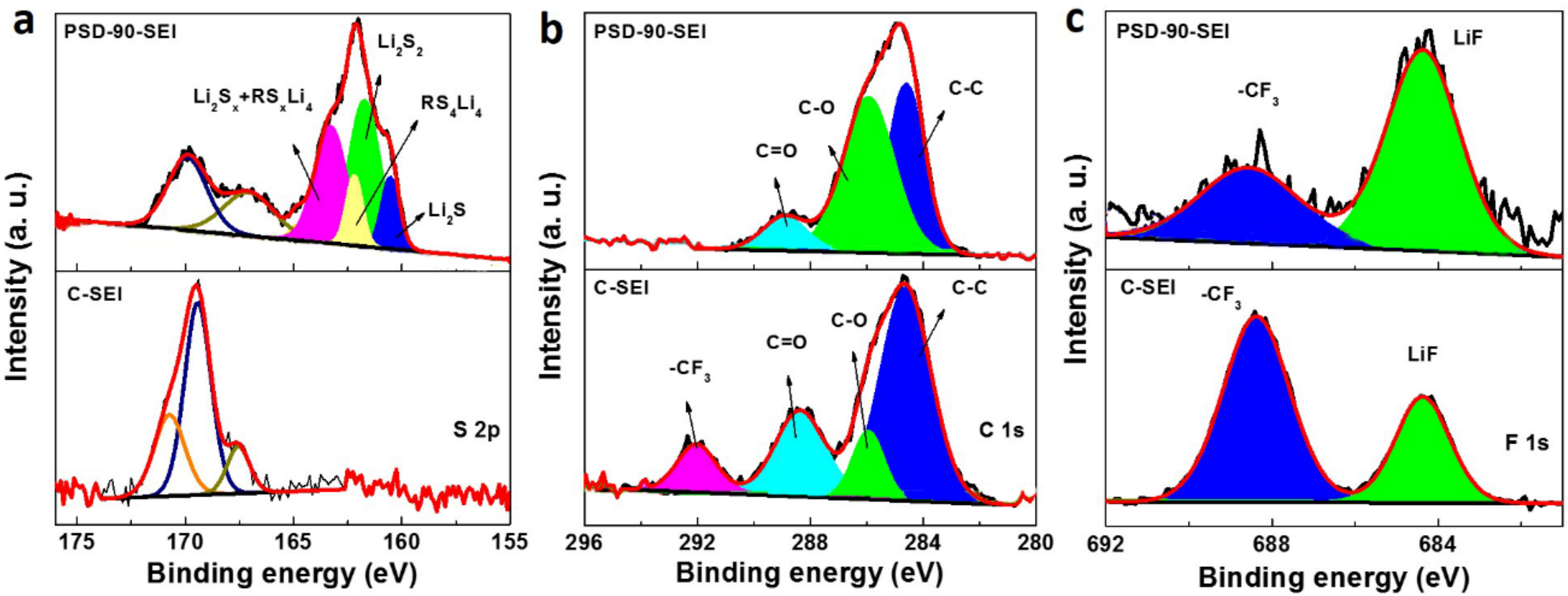
The 2nd generation of organo-Li_xS_y protection layer for Li metal



XPS spectra of the SEI layers

Organo-sulfide present in the SEI layers and decreased content of carbon-fluoride compound in the SEI layers

Technical Accomplishments and Progress

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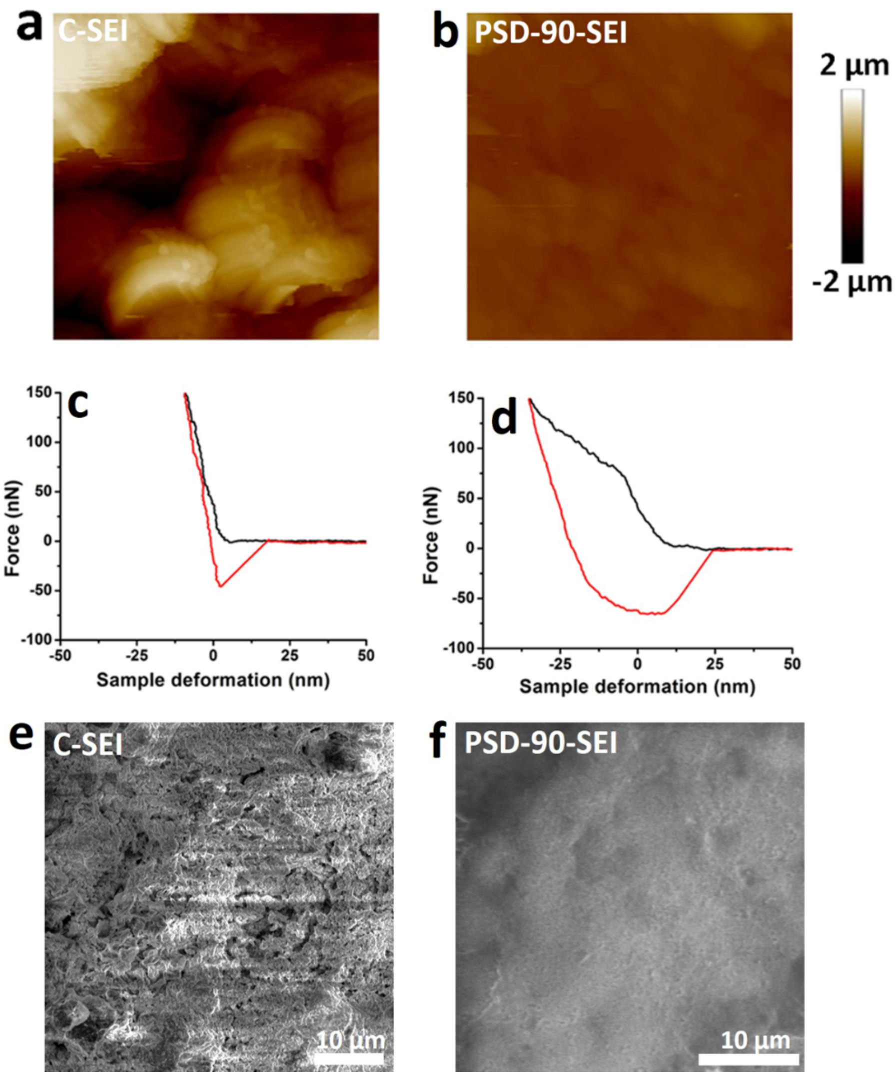
Mechanical properties of the 2nd generation of organo-Li_xS_y protection layer for Li metal



Electrolyte	SEI layer	Reduce modulus (JKR model)/MPa
Control electrolyte	Inorganic layer	903
SCP in electrolyte	Inorganic/organic layer	340

The reduced modulus of organosulfide-plasticized SEI layers

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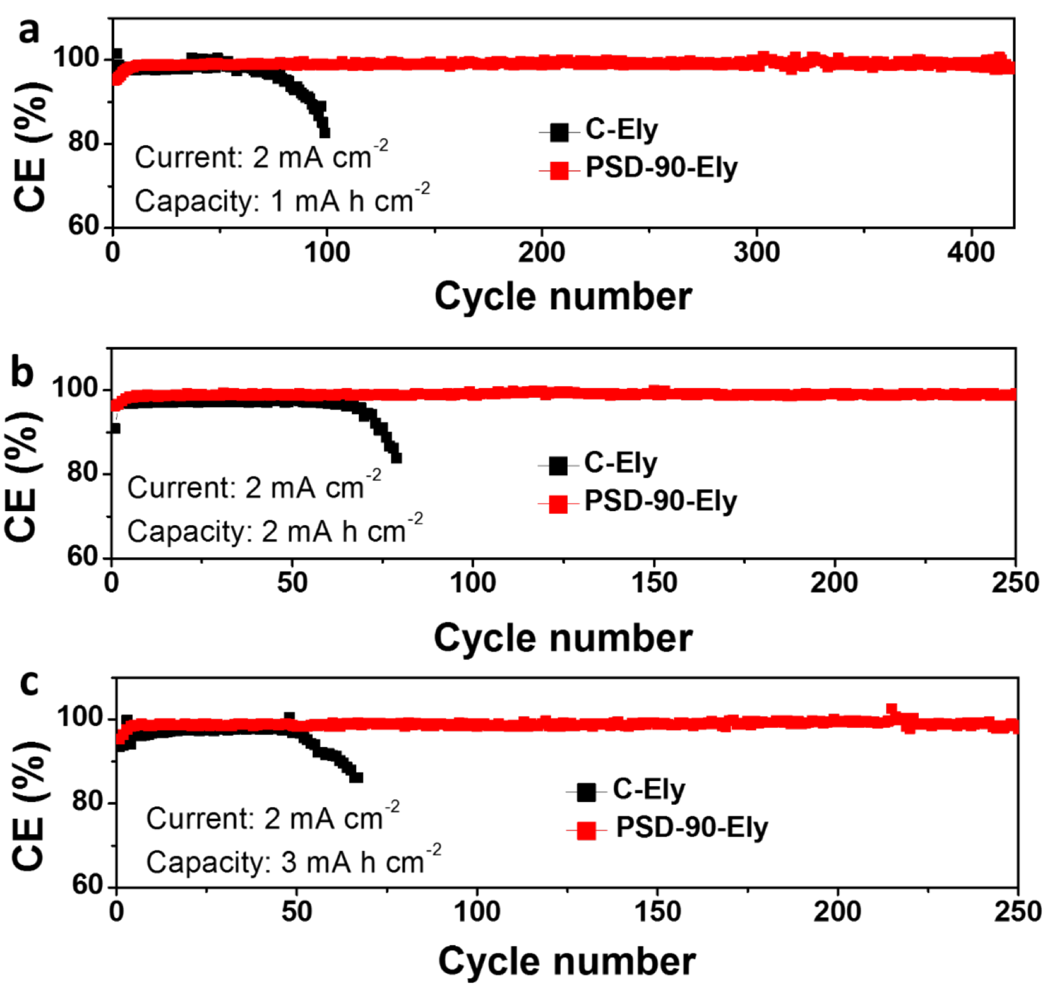
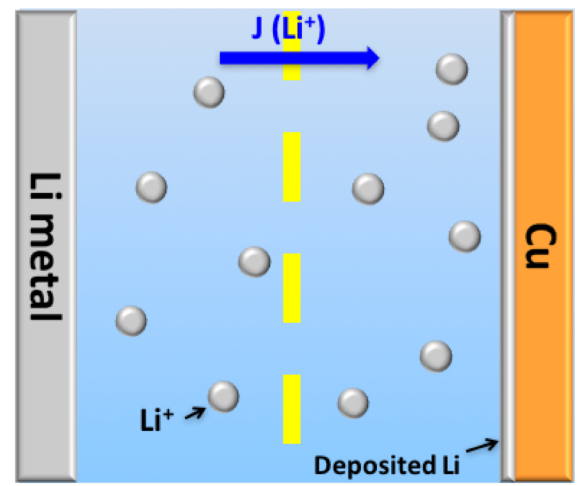
High Li plating/striping efficiency using the 2nd generation of organo-Li_xS_y protection layers





Li | Cu cells for plating/stripping test

2 mA cm^{-2} and 1 mA h cm^{-2} : 99.1% over 420 cycles.
2 mA cm^{-2} and 2 mA h cm^{-2} : 99% over 250 cycles.
2 mA cm^{-2} and 3 mA h cm^{-2}: 98.9% over 250 cycles

Technical Accomplishments and Progress

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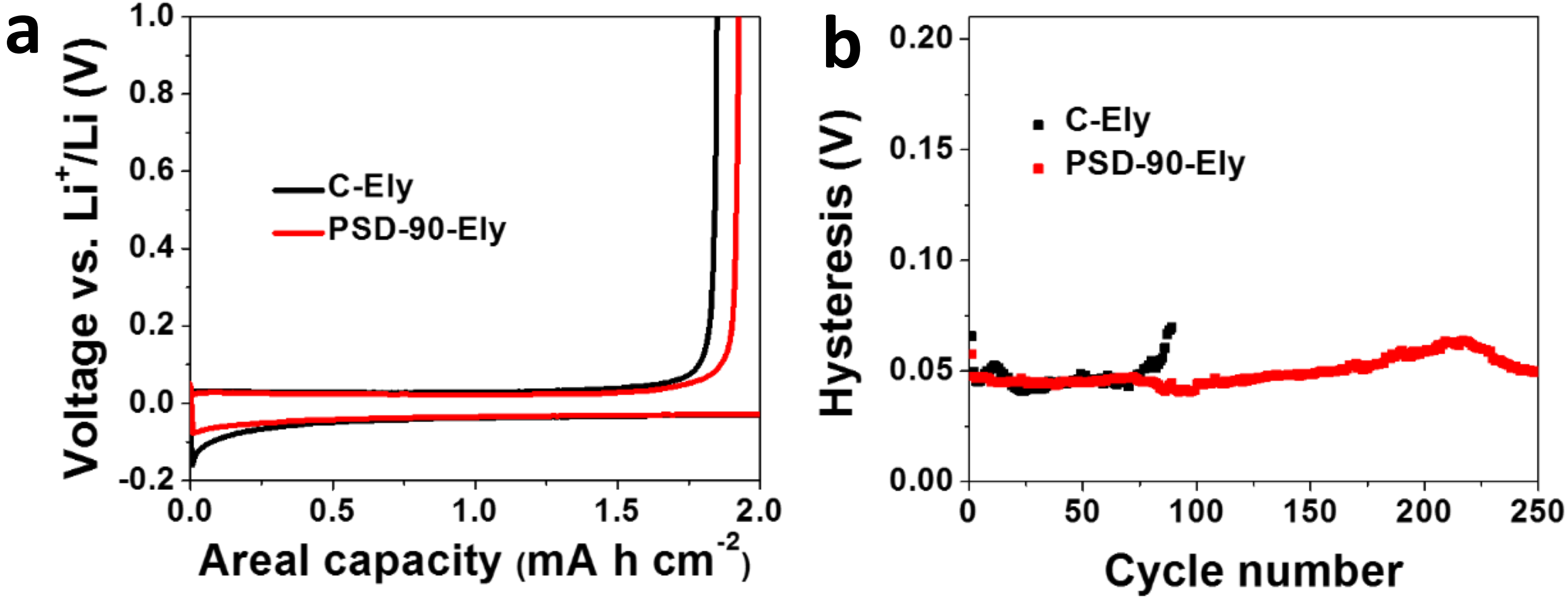
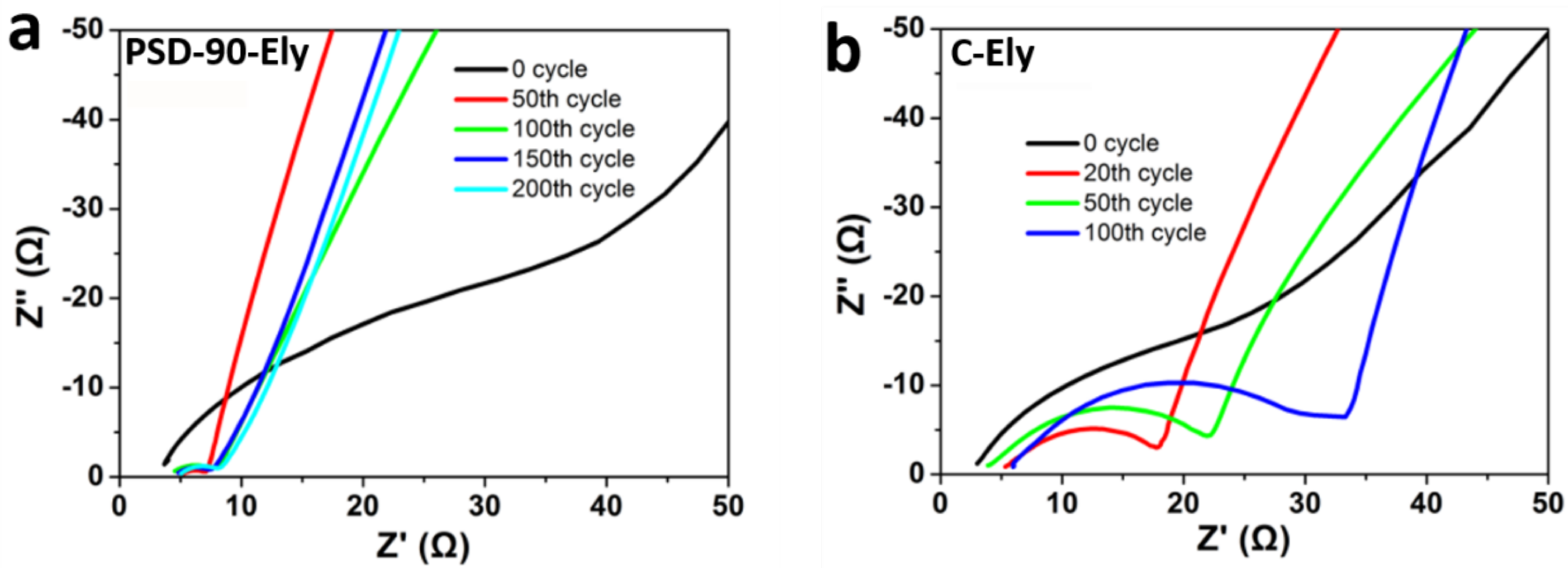


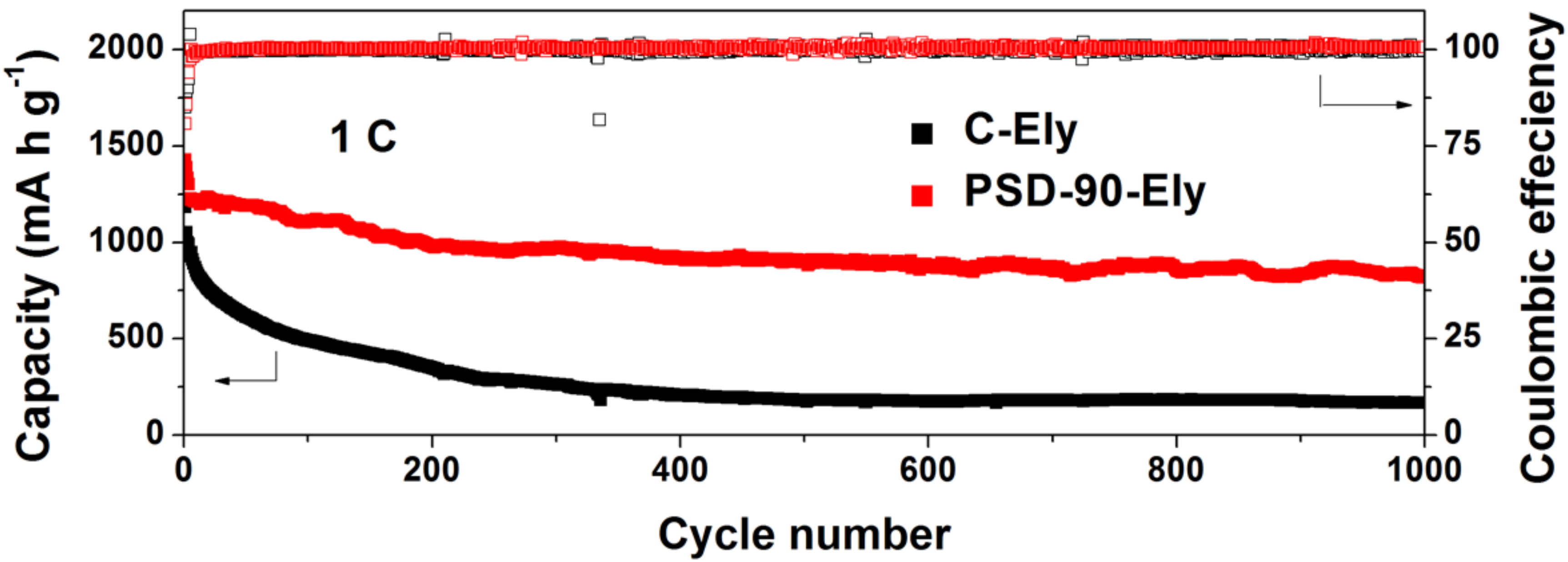
Voltage profiles and average voltage hysteresis of the cells using electrolyte containing different additives. (**a**) Voltage profiles and (**b**) average voltage hysteresis of the Li plating/stripping process with Li metal as the reference/counter electrode at a current density of 2 mA cm^{-2} with a deposition capacity of 2 mA h cm^{-2} using control electrolyte (black symbols) and PSD-90-Electrolyte (red symbols). The voltage profiles are obtained at the first cycle of Li plating/striping.

Technical Accomplishments and Progress



The electrochemical impedance spectra of the cells using different electrolytes after different cycles of Li plating/stripping. (**a**) The cell using the PSD-90-Electrolyte. (**b**) The cell using the control electrolyte. The Li was completely stripped before the EIS characterization.

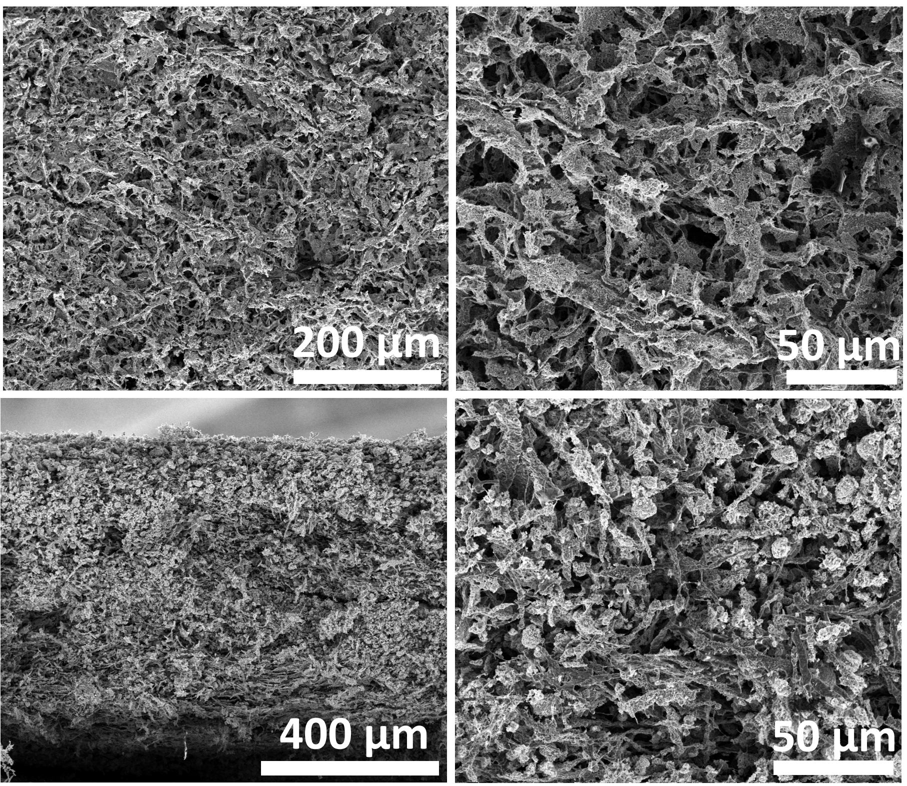
Technical Accomplishments and Progress



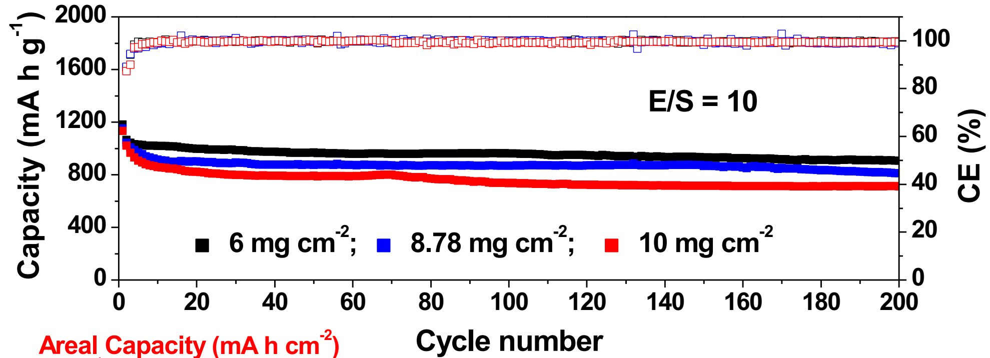
The electrochemical cycling stability of the Li-S cells using control electrolyte (C-Ely) and the 2nd generation of organo-sulfide containing electrolyte (PSD-90-Ely) at a rate of 1 C, respectively. Carbon-sulfur composites containing 70 wt% S were used as the cathode materials.

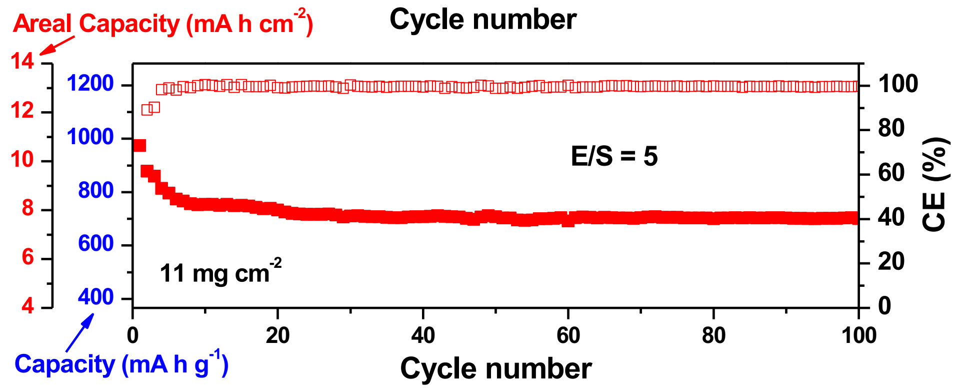
2. Sulfur cathodes

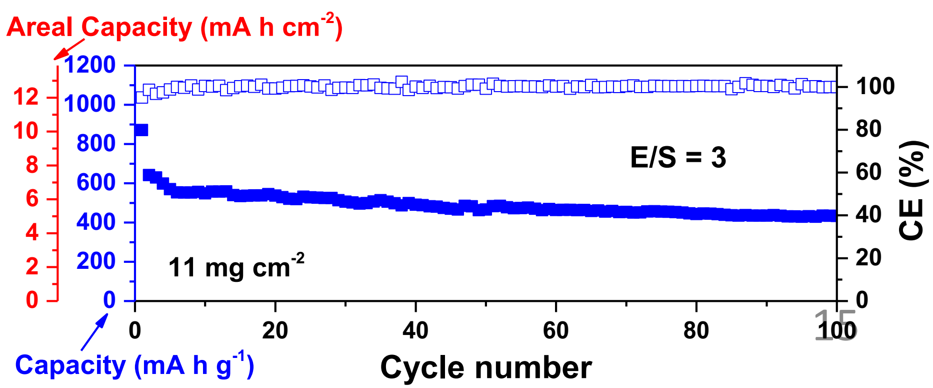
New cathodes enable stable Li-S cells cycling with high sulfur mass loading and at low E/S ratio



Top view and cross-sectional views of the sulfur cathodes







Responses to Previous Year Comments

This project was not reviewed last year.

Partners/Collaborators

- Collaboration with Dr. Seungjin Kim at PSU on AFM characterization of the SEI layers (outside VT program)
- Collaboration with Dr. Long-Qing Chen at PSU on modeling Li dendrite growth under the SEI layer (within VT program)
- Collaboration with Dr. Jun Liu at PNNL on fabrication of Li-S batteries (within VT program)

Remaining Challenges and Barriers

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- Finding appropriate organic and inorganic compositions and developing appropriate synthesis and fabrication methods to prepare inorganic-organic hybrid Li-ion conductor.
- Finding appropriate balance of physical/chemical properties and synthesizing well-structured inorganic-organic hybrid lithium protection layers.
- Ensuring the component compatible with other cell components.
- Achieving high Coulombic efficiency for lithium deposition/dissolution at high deposition capacity and current densities.

Proposed Future Work

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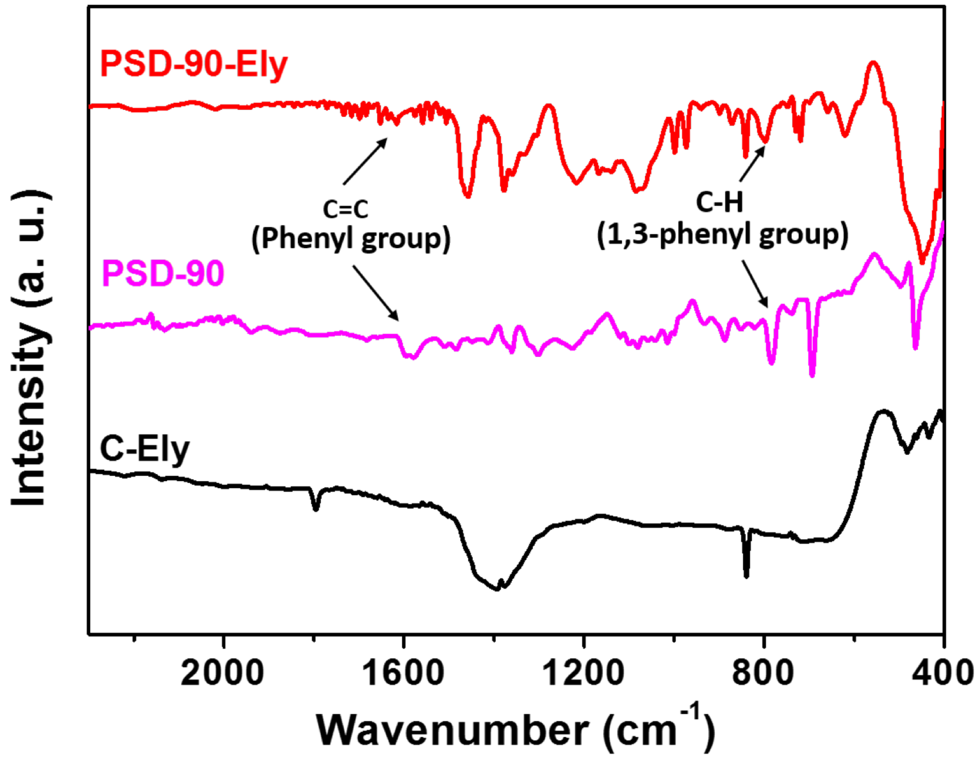
Ongoing (FY18)	Demonstrate the uniform and dendrite-free Li deposition under the protection of 2nd generation organo-Li_xS_y lithium protective layers. (In progress)
	Optimize 2nd generation organo-Li_xS_y lithium protective layer and demonstrate Li anodes cycling with ~98.8% CE for ~200 cycles. (Q3)
	Demonstrate Li anodes with optimized 2nd generation organo-Li_xS_y lithium protective layer and ~99.2% CE for ~300 cycles. (Q4)
Proposed (FY19)	**New Hybrid Organo-Li_xS_y/Organo-$Li_xP_yS_z$ Composite Protection Layer Development**: (1) Organic functional group synthesis and property optimization. (2) Sulfide component synthesis, composition, and structure optimization. (3) Inorganic-organic hybrid composition optimization. (4) Organo-Li_xS_y and Organo-$Li_xP_yS_z$ composition optimization. (5) Protective layer fabrication optimization. (6) Organo-Li_xS_y/Organo-$Li_xP_yS_z$ structure and property characterization. **Performance and Compatibility Testing:** (1) Compatibility testing. (2) Electrochemical testing in coin cells.

Summary

- New generation of sulfur containing polymer with aromatic-based organic components make organo-Li_xS_y lithium protection layers more stable and flexible.
- Stable 2nd generation of organo-Li_xS_y lithium protection layers effectively suppress growth of dendrite Li and significantly improve the Li plating/stripping CE and cycling life.
- Optimize hybrid protective layer and demonstrate Li anodes cycling with ~99.1% CE at 2 mA/cm^2 and 1 mAh/cm^2 capacity for ~420 cycles.
- Novel cathodes with high sulfur mass loading (11 mg cm^{-2}) delivers good cycling performance at low E/S ratio.

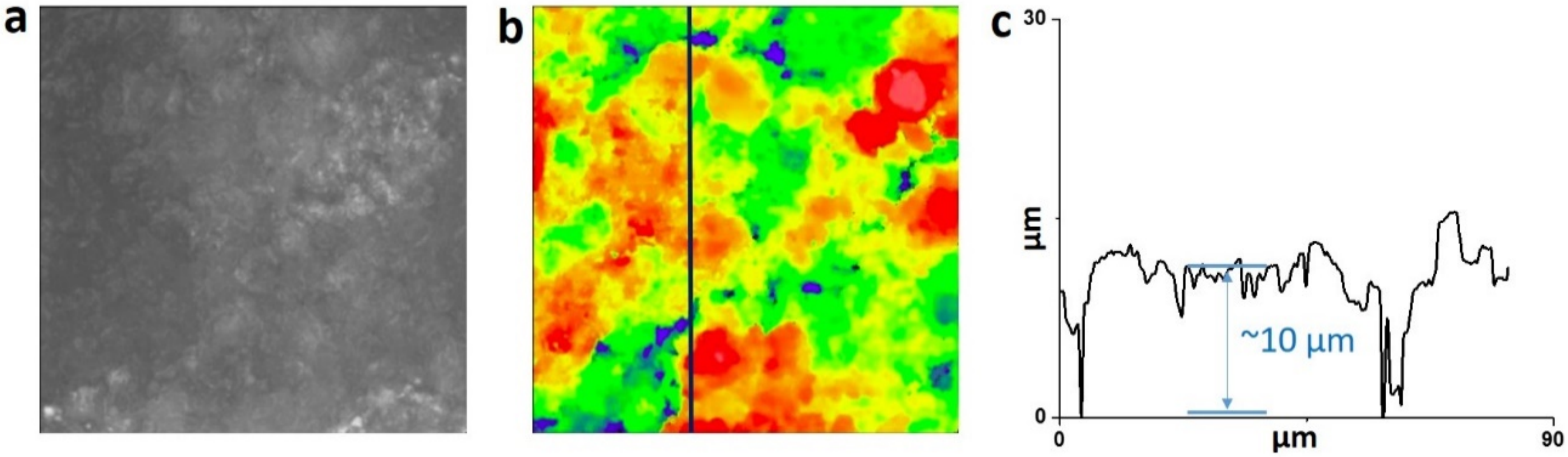
Technical Back-Up Slides

Technical Back-Up Slides



FT-IR of SEI layers obtained from the control electrolyte (C-SEI) and the PSD-90-Electrolyte (PSD-90-SEI). The data indicates the existence of organosulfide/organopolysulfide originating from the PSD-90 in the SEI layer.

Technical Back-Up Slides



Thickness and coverage degree of SEI layer formed from PSD-90-Ely electrolyte. (a) Optical microscope images of PSD-90-SEI layer. (b) Optical profilometry images of PSD-90-SEI layer. (c) Cross-section line profile of PSD-90-SEI layer. The plot in cross-section line profile corresponds to the black line in optical profilometry image. The height from valley to high plateau (marked in c) represents the average film thickness of the SEI layer.